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An improved vdW-type component mixing-rule applied in CO₂-crude system

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Abstract: A new vdW-type mixing-rule has been proposed considering the interaction among the affecting factors of temperature, pressure and non-hydrocarbon components, through analysis of equation of state and theory of interaction among molecules. By the derivation of the formulation at reduced state, a new mixing-rule has been established for the conditions of high pressure and high temperature. The theoretical strictness of the rule has been demonstrated through reducing to the dependency relationship of second virial coefficients. With the in situ petroleum samples data of vapor and liquid phase components from actual measurement, comparison has been taken between the calculation precisions of components and densities parameters calculated by the new rule and the old one. The new mixing-rule has a better accuracy to meet the industrial requirement, and its calculation is also simplified. The weighted mean error of components calculation declines from 15% to 4% and that of density calculation from 10% to 3%.

Key words: CO₂-crude system; state equation; mixing-rule; reference state; flashing calculation; fugacity equation

Introduction

Phase behavior research is an important means to analyze and cognize a gas/liquid system[1–3], in which the interaction between components and phases are studied and mixing rules are introduced or applied to deal with the calculation methods and physical quantity of actual measurement and abstraction.

A large number of studies have been done on mixing rules since the emergence of van de Waals (vdW) equation of state (EOS). These mixing rules can be divided into four main types according to the forms of application and theoretical basis: virial type, vdW type[4–5], interaction parameters related to composition type[6], and local composition based on excess free energy type[7–9].

Each of them has advantages and disadvantages: Virial type, with too many parameters hard to obtain from experimental regression, and the secondary truncation virial function in common use, is only appropriate for fluids with low density; vdW type, normally applied in weak non-ideal system, doesn't give full consideration to HTHP conditions; interaction parameters related to composition type only modifies gravitational parameter and can not return to the form of the second virial coefficient, so it is not rigorous in theory and has "Michelsen-Kistenmacher syndrome"[10]; local composition based

based on excess free energy type can not return to the form of the second virial coefficient and is too complicated in calculation to be applied in actual situation.

As a typical non-ideal system with HTHP, CO₂-crude system has higher requirement on mixing rules[11]. This paper proposed an improvement method on vdW type mixing rule, which not only accords with the independence relationship of the second virial coefficient, but also makes the calculation simpler, and reaches industry precision in calculation of phase behavior.

1. EOS of mixtures

The aim of phase behavior calculation is to find out the relationship between volume and pressure of a system at a certain temperature. This process is described by EOS. Simple in form, easy in calculation and high in accuracy, Soave- Redlich-Kwong (SRK)[12–13] and Peng-Robinson (PR)[14] EOS belonging to cubic EOS are commonly used to describe the relationship between volume and density of CO₂-crude system. Their uniform function form is as follows:

$$p = \frac{RT}{v-b} - \frac{a(T)}{(v+ub)(v+wb)} \tag{1}$$

Formula (1) is based on the study of pure substance and

obtained through theoretical assumption and experimental data. For actual systems with multiple components, since there are interactions between different components, this formula can't be used directly, and mixing rules of components need to be introduced.

2. vdW type mixing rule and modification

The existing mixing rules can not meet the requirements of easy calculation, strict theory and industry precision simultaneously in phase behavior calculation of CO_2-crude system at HTHP[4–9]. Through study, the vdW type mixing rule with terse form and simple computation has been modified to make it suitable for phase parameter calculation of non-hydrocarbon & hydrocarbon systems at HTHP.

2.1. Existing vdW type mixing rule

The form of vdW type mixing rule is as follows:

$$\begin{cases} a_{\mathrm{m}} = \sum_i \sum_j y_i y_j a_{ij} \\ b_{\mathrm{m}} = \sum_i \sum_j y_i y_j b_{ij} \end{cases} \quad (2)$$

The binary mixing rule of vdW type in common use now was improved by Reid from RK mixing rule [15].

$$\begin{cases} a_{\mathrm{m}} = \sum_i \sum_j y_i y_j \left(a_i a_j\right)^{1/2}\left(1-k_{ij}\right) \\ b_{\mathrm{m}} = \sum_i y_i b_i \end{cases} \quad (3)$$

Virial type mixing rule is based on strict statistical mechanics and the qth dimension virial coefficient can be derived as q terms of mole fraction [16].

$$W_q = \sum_{h_1} \sum_{h_2} \cdots \sum_{h_q} x_{h_1} x_{h_2} \cdots x_{h_q} W_{h_1 h_2 \cdots h_q} \quad (4)$$

Virial type mixing rule is strict in theory, so it is often used to verify the correctness of other binary mixing rules.

2.2. Improved vdW type mixing rule

vdW type has been improved to make it suitable for CO_2-crude system at HTHP.

2.2.1. Improved mixing rule of EOS

In CO_2-crude system, the components have different polarity and symmetry, so l_{ij} is introduced to describe polarity and symmetry differences of the components; d_{ij} is used to describe pressure effect; e_{ij} is used to describe temperature effect. Then the new mixing rule is written as.

$$\begin{cases} a_{\mathrm{m}} = \sum_i \sum_j y_i y_j \left(a_i a_j\right)^{1/2}\left(1-k_{ij}\right) e_{ij} \\ b_{\mathrm{m}} = \sum_i \sum_j y_i y_j \left[\left(b_i + b_j\right)/2\right]\left(1-d_{ij}\right) l_{ij} \end{cases} \quad (5)$$

The strictness of the new mixing rule can be verified through converting it into the form of the second virial coefficient as known from the discussion above. The second virial coefficient of cubic EOS can be expressed as $B_m=b_m-a_m/RT$. Substituting Formula (5) into the above formula, we get

$$B_{\mathrm{m}} = \sum_i \sum_j y_i y_j \left\{\left[\left(b_i+b_j\right)/2\right]\left(1-d_{ij}\right)l_{ij} - \frac{\left(a_i a_j\right)^{1/2}\left(1-k_{ij}\right)e_{ij}}{RT}\right\} = \sum_i \sum_j y_i y_j B_{ij} \quad (6)$$

The result shows that formula (6) is the special form of Formula (4) when $q=2$, therefore, the improved mixing rule meets the theoretical strictness.

2.2.2. Improved mixing rule of corresponding state and other physical quantities

Corresponding state has been introduced to deal with the property differences of different components in the mixture system at HTHP. Parameters of different components would be evaluated after converted into the same reference frame to reduce the effect of different property[17].

The following formula is obtained by converting EOS into corresponding state.

$$p_{\mathrm{r}} = \frac{T_{\mathrm{r}}}{A v_{\mathrm{r}} - \Omega_b} - \frac{\Omega_a \alpha(T)}{\left(A v_{\mathrm{r}} + u \Omega_b\right)\left(A v_{\mathrm{r}} + w \Omega_b\right)} \quad (7)$$

Pressure, temperature and compressibility factor should be mixing calculated in description of mixtures with corresponding state equation.

The total mole fraction general formula of RK equation is converted into the following form when applied in description of mixture.

$$z_{\mathrm{m}} = \frac{v_{\mathrm{m}}}{v_{\mathrm{m}} - b_{\mathrm{m}}} - \frac{\Omega_a}{\Omega_b} \frac{b_{\mathrm{m}}}{v_{\mathrm{m}} + b_{\mathrm{m}}} F_{\mathrm{m}} \quad (8)$$

PR and SRK equations are converted into the total mole fraction general formula form by referring to the total mole fraction general formula form of RK equation.

$$z_{\mathrm{m}} = \frac{v_{\mathrm{m}}}{v_{\mathrm{m}} - b_{\mathrm{m}}} - \frac{\Omega_a}{\Omega_b} \frac{b_{\mathrm{m}}}{v_{\mathrm{m}} + b_{\mathrm{m}} + g(v_{\mathrm{m}})} F_{\mathrm{m}} \quad (9)$$

where

$$b_{\mathrm{m}} = \sum_i \sum_j y_i y_j \left[\left(b_i + b_j\right)/2\right]\left(1-d_{ij}\right) l_{ij}$$

The improved item, $g(v_{\mathrm{m}})$, is the function of v_{m}. In SRK equation, $g(v_{\mathrm{m}})=0$; in PR equation, $g(v_{\mathrm{m}})=b_{\mathrm{m}}-b_{\mathrm{m}}/v_{\mathrm{m}}$. In SRK equation, F_{m} is expressed as follows.

$$F_{\mathrm{m}} = \frac{\sum_i \sum_j y_i y_j \left(1-k_{ij}\right) e_{ij}\left\{\left[T_{ci}T_{cj}\big/\left(p_{ci}p_{cj}\right)\right]F_i F_j\right\}^{1/2}}{\sum_j y_j T_{cj}\big/p_{cj}} \quad (10)$$

where

$$F_i = \left(1/T_{ri}\right)\left[1+\left(0.480+1.574\omega_i-0.171\ 5\omega_i^2\right)\left(1-T_{ri}^{1/2}\right)\right]^2$$

$$F_j = \left(1/T_{rj}\right)\left[1+\left(0.480+1.574\omega_j-0.171\ 5\omega_j^2\right)\left(1-T_{rj}^{1/2}\right)\right]^2$$

In PR equation, F_{m} is as same as Formula (10).

$$F_i = \left(1/T_{ri}\right)\left[1+\left(0.374\ 64+1.542\ 26\omega_i-0.269\ 92\omega_i^2\right)\left(1-T_{ri}^{1/2}\right)\right]^2$$

$$F_j = \left(1/T_{rj}\right)\left[1+\left(0.374\ 64+1.542\ 26\omega_j-0.269\ 92\omega_j^2\right)\left(1-T_{rj}^{1/2}\right)\right]^2$$

When acentric factor is large, then